Halogen Compounds

A-Level Chemistry ▪ Topic 15

A-Level Chemistry

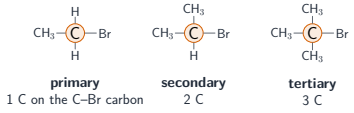
What we will cover

1. Three classes
2. Nucleophilic substitution
3. Substitution vs elimination
4. S_N1 & S_N2
5. Different reactivities

volatile halogenoalkanes

1 Halogenoalkanes

Three classes



primary
1 C on the C–Br carbon

secondary
2 C

tertiary
3 C

A **halogenoalkane** 卤代烷 has a C–X bond.

- **primary** 伯 – 1 carbon on the C–X carbon
- **secondary** 仲 – 2
- **tertiary** 叔 – 3

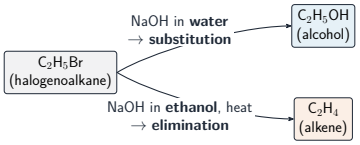
Nucleophilic substitution

The polar carbon is attacked by a **nucleophile** 亲核试剂:

- NaOH(aq) → an **alcohol** 醇
- KCN → a **nitrile** 腈 (adds a carbon)
- NH_3 → an **amine** 胺

Warm with **silver nitrate** 硝酸银 to identify the halogen.

Substitution vs elimination



The conditions decide:

- NaOH in water → substitution (alcohol)
- NaOH in ethanol, heat → **elimination** 消去 (alkene)

2 Mechanism and rate

S_N1 and S_N2

S_N2: one step

$$Nu^- + C\text{–}X \rightarrow [Nu\cdots C\cdots X]^{\ddagger} \rightarrow Nu\text{–}C + X^-$$

rate depends on both reactants — transition state

S_N1: two steps

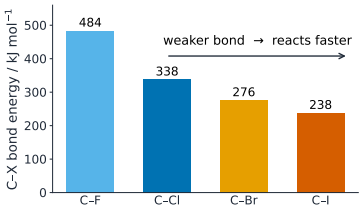
$$C\text{–}X \rightarrow C^+ + X^- \xrightarrow{Nu^-} Nu\text{–}C$$

rate depends on R–X only — carbocation

- **S_N2** 双分子 – one step, a crowded **transition state** 过渡态; primary
- **S_N1** 单分子 – two steps via a **carbocation** 碳正离子; tertiary

The inductive effect stabilises the tertiary carbocation.

Different reactivities



Reactivity depends on the C–X **bond energy** 键能.

> The weaker the bond, the faster it reacts – so iodoalkanes react fastest, chloroalkanes slowest.

3 Recap

Worked example – S_N1 or S_N2?

Predict the mechanism for hydrolysis of (a) 1-bromobutane and (b) 2-bromo-2-methylpropane.

- (a) Primary: little steric hindrance, and a primary cation is too unstable to form.
- ⇒ S_N2: one step, OH^- attacks as Br leaves; rate = k[RBr][OH^-].
- (b) Tertiary: bulky groups block attack, but the tertiary cation is stable.
- ⇒ S_N1: two steps via the cation; rate = k[RBr] only.

> Primary → S_N2, tertiary → S_N1, secondary → both. The rate equation is the exam's proof of which one ran.

Topic 15 – key takeaways

1. **Classes** — primary, secondary, tertiary
2. **Substitution** — NaOH(aq), KCN, NH_3 replace the halogen
3. **Mechanism** — S_N2 (primary) vs S_N1 (tertiary)
4. **Reactivity** — weaker C–X → faster; iodo fastest

Check yourself

1. NaOH in water gives which product?
2. NaOH in ethanol gives which product?
3. Which mechanism do tertiary halogenoalkanes favour?
4. Which halogenoalkane reacts fastest?

Answers **1.** an alcohol **2.** an alkene **3.** S_N1 **4.** the iodoalkane